

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE November 1999		3. REPORT TYPE AND DATES COVERED Final Report	
4. TITLE AND SUBTITLE The Aging Process in Polymers, Positron Annihilation Lifetime Studies				5. FUNDING NUMBERS DAAH04-93-G-0069	
6. AUTHOR(S) John D. McGervey and Alex M. Jamieson					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Case Western Reserve University Cleveland, Ohio 44106-7221				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 30748.11-MS	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Our research effort on this project investigated the capability of positron annihilation lifetime (PAL) spectroscopy to characterize quantitatively the molecular-level structural disorder in the amorphous phase of polymer materials and to enhance our understanding of the relationships between molecular disorder and the functional properties of such materials. A particular interest was to characterize the change in free volume during isothermal annealing, which is the origin of the well-known physical aging effect in mechanical properties of polymeric glasses such as embrittlement.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	
				20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

19991215 038

The Aging Process in Polymers, Positron Annihilation Lifetime Studies

P.I. John D. McGervey, Department of Physics

Co-P.I. Alex M. Jamieson, Department of Macromolecular Science and Engineering

Case Western Reserve University
Cleveland, Ohio

Final Technical Report

Our research effort on this project investigated the capability of positron annihilation lifetime (PAL) spectroscopy to characterize quantitatively the molecular-level structural disorder in the amorphous phase of polymer materials and to enhance our understanding of the relationships between molecular disorder and the functional properties of such materials. A particular interest was to characterize the change in free volume during isothermal annealing, which is the origin of the well-known physical aging effect in mechanical properties of polymeric glasses such as embrittlement. Thermalised positrons, following injection into a polymeric material from a radioactive source such as Na^{22} , are annihilated in one of three mechanisms¹: (a) formation and self-annihilation of parapositronium (pPs), with probability I_1 and lifetime τ_1 ; annihilation as free positrons (e^+), with probability I_2 and lifetime τ_2 ; and formation and 'pick-off' annihilation of oPs, with probability I_3 and lifetime τ_3 . Theoretical arguments,^{2,3} and much circumstantial evidence from several laboratories⁴⁻⁸ has shown that there is a relationship between the oPs annihilation parameters, I_3 and τ_3 , and the free volume characteristics of amorphous polymers. Specifically, I_3 , which is a measure of the probability of oPs formation, appears to be proportional to the number of free volume holes, and τ_3 is related to the hole radius, R , by an equation of the form^{2,3}:

$$\tau_3 = 0.5[1 - R/R_0 + (\sin 2\pi(R/R_0)/2\pi)]^{-1}$$

where R_0 is an empirical parameter. Our first task was to make quantitative comparisons between free volume parameters extracted from oPs annihilation lifetime spectra and an independent estimate of free volume. In our investigations⁹⁻²⁰, we used a free volume function, $h(P,T)$, extracted from PVT data for the polymer chosen for study, using a statistical mechanical model due to Simha and Somcynski²¹. With this approach, we were able to demonstrate excellent quantitative agreement between a fractional free volume, f , estimated from oPs data via the equation:

$$f = K I_3 (4/3\pi R^3),$$

where K is an empirical constant, and the theoretical $h(P,T)$ function in the equilibrium melt for several pure polymers⁹⁻¹³, including polyvinylacetate⁹, the polycarbonate of bisphenol A¹⁰⁻¹², and polystyrene¹³. Most interestingly, significant deviations were found in the non-equilibrium glassy state, which were traced to deficiencies in the theory¹³. Thus, an empirical free volume function, numerically consistent with the statistical h -function in the melt, was found to be quantitatively consistent with the oPs f -values in both melt and glass¹³⁻¹⁵. We were thus the first to definitively establish a quantitative correlation between a well-defined theoretical free volume function and o-PS annihilation lifetime parameters I_3 and τ_3 in both melt and glass.

For the above polymers, as well as certain well-specified miscible polymer blends, it was further established that a correlation exists between the oPs free volume and bulk properties, such as physical aging of stress relaxation¹⁶, and the composition dependence of the glass transition temperature¹⁷. The latter study¹⁷ is particularly interesting because, using oPs annihilation parameters, we were able to validate a well-known theoretical argument that the composition dependence of the glass transition temperature of an athermal miscible blend, for which the volume change on mixing is also close to zero, can be predicted based on the free volume characteristics of the pure components. Changes in free volume on cross-linking elastomers were investigated and universal scaling parameters for free volume parameters at the glass transition temperature were described¹⁸. The temperature-dependence of free volume was measured in two commercially-important, wholly-aromatic copolyesters of hydroxybenzoic acid and hydroxynaphthoic acid, and their blends¹⁹. At room temperature, I_3 and τ_3 were exceedingly small compared to typical amorphous flexible polymers, but each showed a very large increase with temperature up to the melting point. The onset of the increase in oPs free volume was observed at a temperature in the solid state where there is a transition in mechanical properties. The unusually small values of τ_3 may reflect the fact that the free volume holes in these fibrous polymers are prolate rather than spherical in shape, since theory suggests that the annihilation lifetime of prolate holes is determined by the shorter dimension.

We were the first to carry out an *in situ* PAL study of free volume changes in a glassy polymer (polycarbonate) under well-specified tensile deformation, using a custom-built miniature load cell²⁰. The oPs free volume increased with applied strain in a fashion numerically consistent with that calculated from the above-mentioned empirical free volume function of Simha-Somcynsky²¹ based on the known value of the Poissons ratio for polycarbonate. This gives us confidence that the PAL method can be applied to probe changes in the structural disorder of the amorphous component in polymer composites and stiff-chain polymers induced by mechanical deformation or other physical perturbations.

There is great interest in the possibility of using PAL to gain information about the distribution of free volume hole sizes in polymers through analysis of the oPs lifetime distribution. Indeed, a number of reports of such measurements have been published^{22,23}. Several concerns exist with regard to these studies. First, we have proposed theoretical

arguments²⁴ that, because of the possibility of tunneling of oPs between holes, the oPs lifetime distribution may not reflect a complete picture of the hole distribution. Subsequent theoretical analysis²⁵, however, suggests that the tunneling effect may be negligible. Even if this is true, it is not clear that the measured hole size distributions are accurate. For example, the published distributions invariably are based on fits where the quantum mechanically-required ratio between pPs and oPs annihilation probabilities, viz. $I_1/I_3 = 1/3$, is not satisfied. Our own simulations¹¹ of positron annihilation spectra containing distributions of τ_3 values indicate this discrepancy arises because some of the short-lived oPs intensity is being counted as pPs or e^+ in the fitted spectra. Moreover, the same simulations indicate that, if the time resolution function is as large as 260 psec, as typical for most of these studies, there will be significant errors in the mean oPs lifetimes and intensities even for spectra with very low noise levels. Moreover, in most of the cited studies of oPs distributions, it is not made clear that the associated spectral fits are statistically better than fits to a single oPs lifetime. If this is not so, then the obtained oPs lifetime distributions do not contain meaningful information. From our modelling studies¹¹, analyses of oPs lifetime distributions are questionable unless one uses a time resolution function with a width below 200 psec, and the above-discussed fitting criteria are met. Note that these considerations do not preclude the application of mean oPs lifetimes to characterise average free volumes. Our simulations demonstrate¹¹ that the loss of short-time oPs information does not introduce significant errors into the mean oPs lifetimes, $\langle \tau_3 \rangle$, which correspond to an intensity-weighted average, $\langle \tau_3 \rangle = \sum I_{3i} \tau_{3i} / \sum I_{3i}$. Finally, to obtain adequate signal to noise ratio for optimal analysis of PAL spectra, it is necessary to record an exceptionally large number of annihilation events which increases the possibility of radiation damage to the specimen²⁶. Such damage results in anomalous behavior of the oPs intensities, but does not affect the mean lifetime measured^{26,27}. It is not clear if such long term radiation damage leads to artifacts in attempts to resolve intensity-based distributions of oPs lifetimes.

In conclusion, we explored the use of oPs lifetime measurements to investigate changes in free volume during physical aging of polymeric materials. Early reports of decreases in the number of free volume holes during isothermal annealing of polystyrene²⁸ and polyvinylacetate⁹, based on an observed decrease in oPS intensity, proved to be due to radiation damage rather than a change in free volume. Subsequently, we carried out measurements on glassy polycarbonate¹⁰ in which the polymer specimen was separated from the positron source during annealing and found a decrease in both oPS lifetime and intensity, which we assign to a true measure of the decrease in free volume associated with the aging process.

References

1. D. M. Schrader, and Y. C. Jean, *Positron and Positronium Chemistry*, Elsevier, New York, 1988.
2. S. J. Tao, *J. Chem. Phys.* 56, 5499 (1972).

3. H. Nakanishi, S. J. Wang, and Y. C. Jean, in Proceedings of the International Conference on Positron Annihilation in Fluids, Arlington, Tx., Eds., S. C. Sharma World Scientific Publishing, Singapore, 1987, p. 252.
4. J. R. Stevens, and S. J. Mao, J. Appl. Phys. 41, 4273 (1970).
5. B. D. Malhotra, and R. A. Pethrick, Macromolecules, 16, 1175 (1983).
6. H. Nakanishi, and Y. C. Jean, J. Polymer Sci. Polym. Phys. 27, 1419 (1989)
7. A. J. Hill, K. J. Heater, and C. M. Agrawal, J. Polym. Sci. Polym. Phys. 28, 37 (1990).
8. L. Xie, D. W. Gridley, H. A. Hristov, and A. Yee, Polymer, 35, 14 (1994).
9. Y. Kobayashi, W. Zheng, E. F. Meyer, J. D. McGervey, A. M. Jamieson, and R. Simha, Macromolecules, 22, 2302 (1989).
10. J. E. Kluin, Z. Yu, S. Vleeshouwers, J. D. McGervey, A. M. Jamieson, and R. Simha, Macromolecules, 25, 5089 (1992).
11. S. Vleeshouwers, J. E. Kluin, J. D. McGervey, A. M. Jamieson, R. Simha, J. Polymer Sci. Polym. Phys., 30, 1429 (1992).
12. J. E. Kluin, Z. Yu, S. Vleeshouwers, J. D. McGervey, A. M. Jamieson, R. Simha, and K. Sommer, Macromolecules, 26, 1853 (1993).
13. Z. Yu, U. Jahse, J. D. McGervey, A. M. Jamieson, and R. Simha, J. Polymer Sci. Polym. Phys. 32, 2637 (1994).
14. H. Higuchi, Z. Yu, A. M. Jamieson, R. Simha, and J. D. McGervey, J. Polym. Sci. Polym. Phys. 33, 2295, (1995).
15. H. Higuchi, A. M. Jamieson, and R. Simha, J. Polym. Sci. Polym. Phys., 34, 1423 (1996).
16. G. W. Cheng, Z. Yu, A. M. Jamieson, and J. D. McGervey, J. Applied Polymer Sci., 63, 483 (1997).
17. Z. L. Peng, B. G. Olson, R. Srithawatpong, J. D. McGervey, A. M. Jamieson, H. Ishida, T. M. Maier, and A. F. Halasa, J. Polymer Sci. Polym. Phys., 36, 861 (1998).
18. R. Srithawatpong, B. G. Olson, Z. L. Peng, A. M. Jamieson, R. Simha, J. D. McGervey, H. Ishida, T. Maier, and A. F. Halasa, J. Polym. Sci. Poly. Phys., in press (1999).

19. C. M. McCullagh, Z. Yu, A. M. Jamieson, J. Blackwell, and J. D. McGervey, *Macromolecules*, **28**, 6100 (1995).
20. M. Ruan, H. Moaddel, A. M. Jamieson, R. Simha, and J. D. McGervey, *Macromolecules*, **25**, 2407 (1992).
21. R. Simha, and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
22. J. Liu, Y. C. Jean, and H. Yang, *Macromolecules*, **28**, 5774 (1995).
23. Y. C. Jean, J. P. Yuan, J. Liu, Q. Deng, and H. Yang, *J. Polymer Science, Polym. Phys.*, **33**, 2365 (1995).
24. Z. Yu, J. D. McGervey, A. M. Jamieson, and R. Simha, *Macromolecules*, **28**, 6268 (1995).
25. A. H. Baugher, W. J. Kossler, and K. G. Petzinger, *Macromolecules*, **29**, 7280 (1996).
26. M. Welfand and F. H. J. Maurer, *Mater. Sci. Forum*, **105-110**, 1811 (1992).
27. Z. L. Peng, B. G. Olson, J. D. McGervey, and A. M. Jamieson, *Polymer*, **40**, 3033 (1999).

List of All Publications

1. Y. Kobayashi, W. Zheng, E. F. Meyer, J. D. McGervey, A. M. Jamieson and R. Simha, *Macromolecules*, **22**, 2302 (1989), "Free Volume and Physical Aging of Poly(Vinyl Acetate) Studied by Positron Annihilation".
2. M. Y. Ruan, H. Moaddel, A. M. Jamieson, R. Simha and J. D. McGervey, *Macromolecules*, **25**, 2407 (1992), "Positron Annihilation Lifetime Studies of Free Volume Changes in Polycarbonate under Static Tensile Deformation".
3. J. E. Kluin, Z. Yu, S. Vleeshouwers, J. D. McGervey, A. M. Jamieson and R. Simha, *Macromolecules*, **25**, 5089 (1992), "Temperature and Time-Dependence of Free Volume in Bisphenol-A Polycarbonate Studied by Positron Lifetime Spectroscopy".
4. S. Vleeshouwers, J. E. Kluin, J. D. McGervey, A. M. Jamieson and R. Simha, *J. Polymer Sci. Polym. Phys.*, **30**, 1429 (1992), "Monte Carlo Calculations of Hole Size Distributions; Simulation of Positron Annihilation Spectroscopy".
5. J. E. Kluin, Z. Yu, S. Vleeshouwers, J. D. McGervey, A. M. Jamieson, R. Simha and K. Sommer, *Macromolecules*, **26**, 1853 (1993), "Ortho-positronium Lifetime Studies of Free Volume in Polycarbonates of Different T_g : Influence of Hole Size Distributions".

6. Z. Yu, U. Jahse, J. D. McGervey, A.M. Jamieson, R. Simha, J. Polymer Sci., Polym. Phys., 32, 2637 (1994), "Effect of Molecular Weight on Orthopositronium Annihilation in Amorphous Polystyrene".
7. Z. Yu, J. D. McGervey, A./ M. Jamieson, and R. Simha, Macromolecules, 28, 6268 (1995), "Can Positron Annihilation Lifetime Spectroscopy Measure the Free Volume Hole Size Distribution in Amorphous Polymers?"
8. C. M. McCullagh, Z. Yu, A. M. Jamieson, J. Blackwell and J. D. McGervey, Macromolecules, 28, 6100 (1995), "Positron Annihilation Lifetime Measurements of Free Volume in Wholly-Aromatic Copolyesters and Blends".
9. H. Higuchi, Z. Yu, A. M. Jamieson, R. Simha and J. D. McGervey, J. Polymer Sci. Polym. Phys., 33, 2295 (1996), "Thermal History and Temperature Dependence of Viscoelastic Properties of Polymer Glasses: Relation to Free Volume Quantities".
10. H. Higuchi, A. M. Jamieson, and R. Simha, J. Polymer Sci. Polym. Phys., 34, 1423 (1996), " Free Volume Quantities and the Viscoelasticity of Polymer Glasses".
11. G. W. Cheng, Z. Yu, A. M. Jamieson, and J. D. McGervey, J. Appl. Polym. Sci. 63, 483 (1997), "Physical Aging in the Mechanical Properties of Miscible Polymer Blends".
12. Z. L. Peng, B. G. Olson, R. Srithawatpong, J. D. McGervey, A. M. Jamieson, H. Ishida, T. M. Maier, and A. F. Halasa, J. Polymer Sci. Polym. Phys., 36, 861 (1998), " Study of Free Volume in High Vinyl-Polybutadiene/cis-Polyisoprene Blends by Positron Annihilation Lifetime Spectroscopy "
13. Z. L. Peng, B. G. Olson, J. D. McGervey, and A. M. Jamieson, Polymer, 40, 3033 (1999), "Temperature and Time Dependence of Orthopositronium Formation in Polystyrene"
14. R. Srithawatpong, B. G. Olson, Z. L. Peng, A. M. Jamieson, R. Simha, J. D. McGervey, H. Ishida, T. Maier, and A. F. Halasa, J. Polym. Sci. Poly. Phys. In press (1999), "Positron Annihilation Lifetime Studies of Free Volume Changes on Cross-Linking cis-Polyisoprene, High Vinyl-Polybutadiene, and Their Miscible Blends"

List of All Scientific Personnel

Principal Investigator J. D. McGervey (Physics, CWRU)

Co-Investigators

A. M. Jamieson (Macromolecular Science, CWRU)

R. Simha (Macromolecular Science, CWRU)

Collaborators

Y. Kobayashi (National Institute of Materials Research, Tsukuba, Japan)
H. Ishida (Macromolecular Science, CWRU)
K. Sommer (Bayer Company, USA)
H. Higuchi (Idemitsu Kosan Co., Chiba, Japan)
T. Maier (Goodyear Tire and Rubber Company, USA)
A. Halasa (Goodyear Tire and Rubber Company, USA)
S. Vleeshouwers (Technical University, Eindhoven, The Netherlands)

Postdoctoral Research Associates

W. Zheng
J. E. Kluin
Z. L. Peng

Graduate Students

E. F. Meyer (PhD, Physics, CWRU, 1989)
H. Moaddel (MS, Macromolecular Science, CWRU, 1991)
M. Ruan (PhD, Physics, CWRU, 1992)
G. W. Chang (PhD, Macromolecular Science, CWRU, 1993)
Z. Yu (PhD, Physics, CWRU, 1995)
U. Jahse (MS, Physics, CWRU, 1994)
G. Carri (MS, Macromolecular Science, CWRU, 1995)
C. M. McCullagh (PhD, Macromolecular Science, CWRU, 1995)
R. Srithawatpong (MS, Macromolecular Science, CWRU, 1998)
B. G. Olson (Physics, CWRU, current student)